

Supporting Information on
Experimental and Theoretical Study on Competitive Adsorption of Aromatic
Compounds on Reduced Graphene Oxides

Shujun Yu^{a,b}, Xiangxue Wang^{a,b}, Yuejie Ai^{a*}, Xiaoli Tan^{b,c}, Tasawar Hayat^{d,e},
Wenping Hu^{f*} and Xiangke Wang^{a,c,e*}

a. School of Environment and Chemical Engineering, North China Electric Power University, Beijing 102206, P. R. China.

b. Key Laboratory of Novel Thin Film Solar Cells, Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, P. R. China.

c. Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, School for Radiological and Interdisciplinary Sciences, Soochow University, Suzhou 215123, P.R. China

d. Department of Mathematics, Quaid-I-Azam University, Islamabad 44000, Pakistan

e. NAAM Research Group, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

f. Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

*: Corresponding authors. xkwang@ncepu.edu.cn (X.K. Wang), Tel(Fax): +86-10-61772890. aiyuejie314@126.com (Y.J. Ai); huwp@iccas.ac.cn (W.Hu).

Synthesis of graphene oxides (GOs) and reduced graphene oxides (rGOs). The GOs were synthesized by chemical oxidation of expanded graphite using modified Hummers method.¹ Typically, 2.0 g of flake graphite (48 μm , 99.95% purity) and 1.5 g NaNO_3 (as co-solvent) were added into a 250 mL round bottom flask, then 150 mL concentrated H_2SO_4 was added under stirring and ice-water bath conditions. Then 9.0 g of the oxidizing agent (KMnO_4) was slowly added into the suspension more than 2 h. The suspension was continually stirred for 5 d at room temperature. Then 280 mL of 5 wt % H_2SO_4 was added and the temperature was kept at 98 $^\circ\text{C}$ for 2 h. 12 mL of H_2O_2 (30 wt %) was added in the suspension when the temperature was reduced to 60 $^\circ\text{C}$. After reactions, the mixture was centrifuged and washed with 10 % H_2SO_4 solution to remove residual metal ions. The precipitate was then washed with distilled water and centrifuged repeatedly until the solution became neutral. The GOs were obtained by centrifuging at 18000 rpm for 60 min after ultrasonic treatment at 400 W for 30 min.

The rGOs were obtained by hydrazine hydrate reduction of GOs under water-cooled condenser conditions.² Briefly, 0.3 g of GOs were dispersed in 40 mL of deionized water under ultrasonication (150 W) until it became clear with no visible particulate matter. Then 1.0 mL of 80 wt % hydrazine hydrate was added into the dispersion under water-cooled condenser conditions, and mixtures were vigorously heated at 100 $^\circ\text{C}$ for 24 h under vigorous stirring conditions. The yellow-brown solution was gradually transferred to black precipitate during the reduction process. The rGOs powder was obtained through centrifugation and freeze drying overnight.

Detection of Ben, BN and NA. Multiple linear regression analysis is the method of statistics in regression that used to analyze the relationship between single response variable (dependent variable) with two or more controlled variables (independent variables).^{3,4} In this research, absorbance was used as response variable, while concentrations of aromatic compounds (Ben, BN and NA) were taken as variables. The concentrations of Ben, BN and NA were analyzed by ultraviolet-visible (UV-vis) spectroscopy at the wavelength of 205, 280 and 236 nm, respectively. The adsorption spectra of these three components severely overlap in the ultraviolet spectral range. Three-wavelength linear regression method was taken to solve this problem. 25 mixture standard resolutions were prepared as orthogonal projection form L_{25} (5⁶). The regression equations are presented in the following equation:

$$A^{205\text{nm}} = 0.0205 C_1 + 0.0183 C_2 + 0.0128 C_3 \quad (1)$$

$$A^{236\text{nm}} = 0.0007 C_1 + 0.0148 C_2 + 0.0139 C_3 \quad (2)$$

$$A^{280\text{nm}} = 0.0003 C_1 + 0.0149 C_2 + 0.0009 C_3 \quad (3)$$

where A is the absorbance values of the solution; C_1 , C_2 and C_3 represent the concentration of Ben, BN and NA, respectively. To verify the applicability of this method, the content of Ben, BN and NA in six simulation mixture samples was measured. The mixture content of simulation samples was shown in Table S3. The measurement results indicated that the analytical results' mean of relative error was less than 5%. The measurement system is stable and reliable.

Adsorption isotherms. The Langmuir isotherm model usually describes the monolayer adsorption process that takes place on a homogeneous surface. It can be

expressed by the following equation:⁵

$$q_e = \frac{bq_{\max}C_e}{1 + bC_e} \quad (4)$$

where q_e (mmol/g) and C_e (mmol/L) are the amount of aromatic compounds adsorption on the adsorbents and concentration of aromatic compounds at solution after equilibrium, respectively. q_{\max} (mmol/g), the maximum adsorption capacity, is the amount of aromatic compounds at complete monolayer coverage, and b (L/mol) is a binding constant that relates to the heat of adsorption.

The Freundlich expression is an exponential equation that represents properly the adsorption data at low and intermediate concentrations on heterogeneous surfaces.⁶ Its form can be expressed as follows:

$$q_e = K_F C_e^n \quad (5)$$

where K_F (mmol¹⁻ⁿ Lⁿ/g) represents the adsorption capacity when the equilibrium concentration of radionuclide equals to 1, and n represents the degree of dependence of adsorption with equilibrium concentration.

Sips isotherm is a combined form of Langmuir and Freundlich expression for the prediction of the heterogeneous adsorption.⁷ At low adsorbate concentration, it reduces to Freundlich isotherm, whereas it predicts a monolayer adsorption capacity characteristic of Langmuir isotherm at high adsorbate concentration. It is expressed as:

$$q_e = \frac{K_s C_e^{n_s}}{1 + a_s C_e^{n_s}} \quad (6)$$

where K_s (L/g) and a_s (L/mmol) is the Sips isotherm constant and n_s is the Sips parameter for surface heterogeneity description.

References

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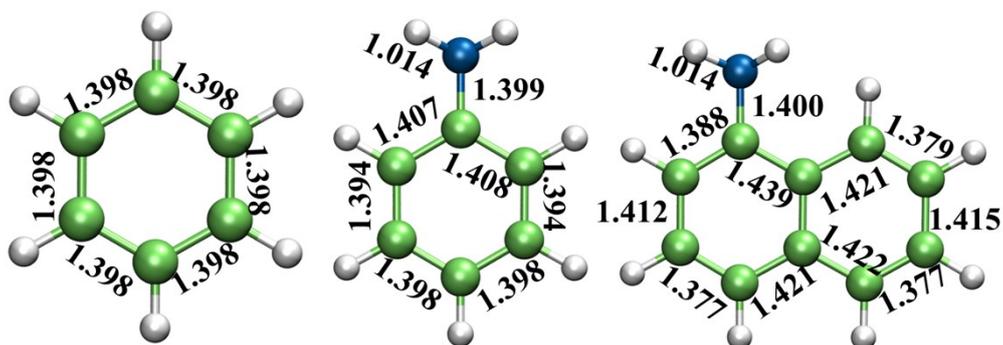


Figure S1. Optimized geometrical parameters for Ben, BN, and NA obtained at the B3LYP/ 6-31G (d)//CPCM level of theory; distances are in angstroms (Å). Color code by atom: green carbon, blue nitrogen, white hydrogen.

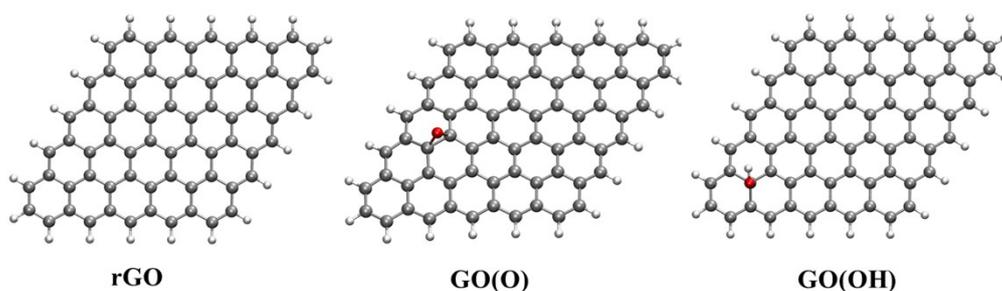
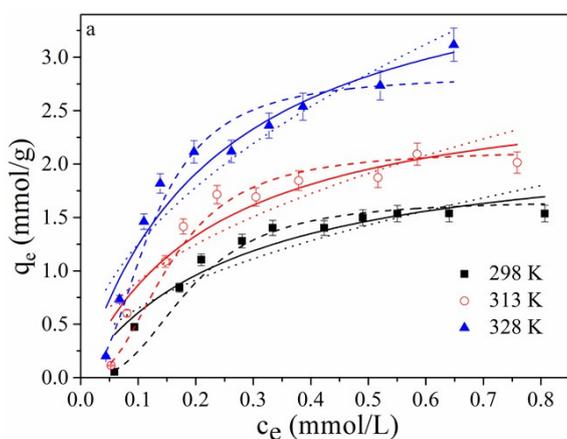


Figure S2. Molecular models for reduced graphene oxides (rGOs) and oxidized graphenes (GO(O) and GO(OH)). The graphene is functionalized on the basal plane with oxygen and hydroxyl groups.



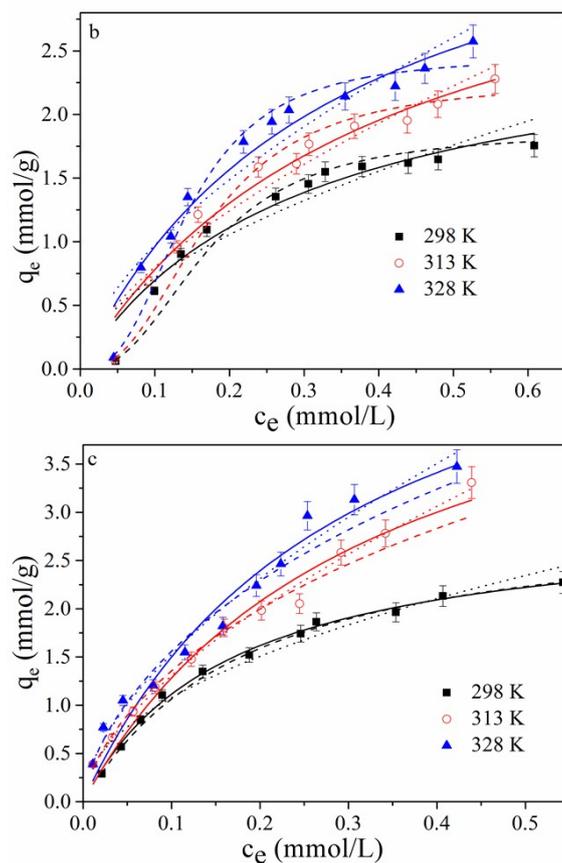


Figure S3. Adsorption isotherms of Ben (a), BN (b) and NA (c) on rGOs. $\text{pH} = 6.5 \pm 0.1$, $I = 0.01 \text{ mol/L NaClO}_4$, $m/V = 0.1 \text{ g/L}$. The solid lines represent the Langmuir model. The dotted lines represent the Freundlich model. The dashed lines represent the Sips model.

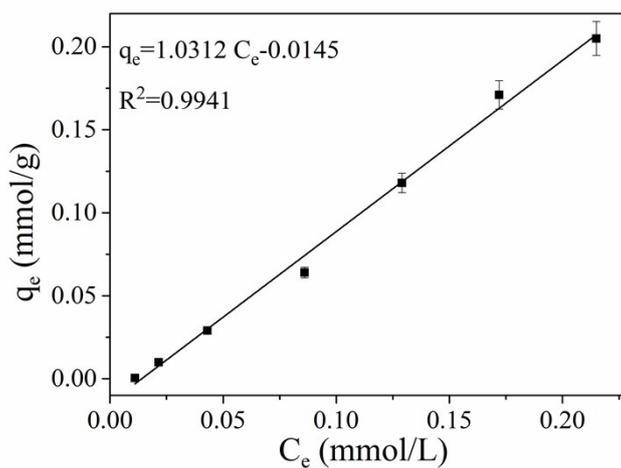


Figure S4. Adsorption isotherm of BN by NA. $\text{pH} = 6.5 \pm 0.1$, $m/V = 0.4 \text{ g/L}$.

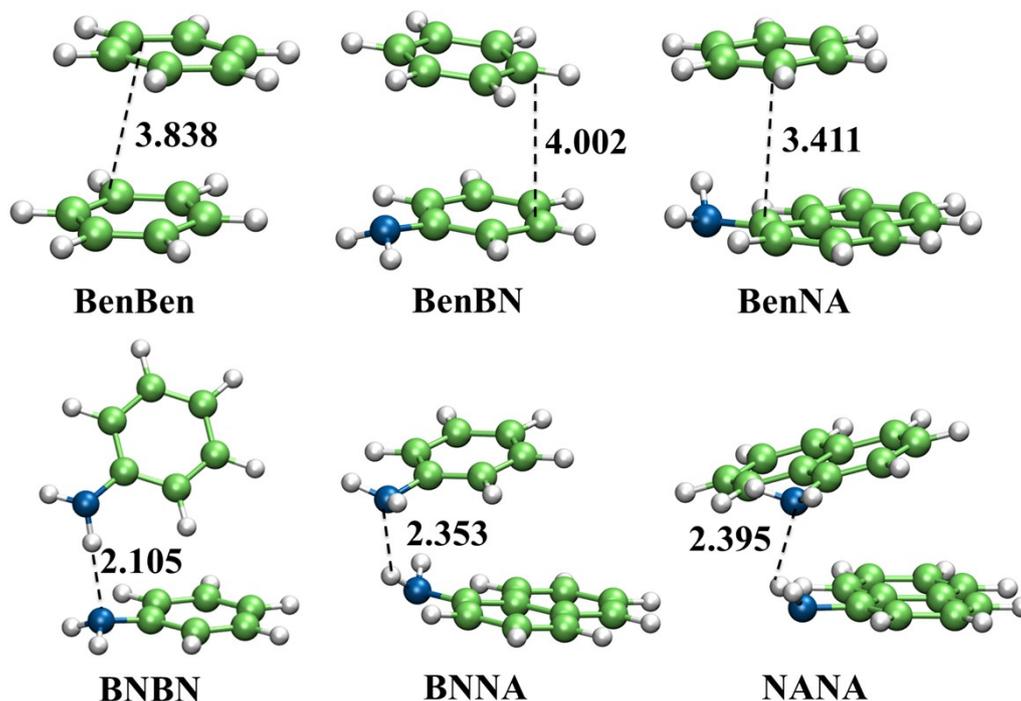


Figure S5. Optimized geometrical parameters for different aromatic dimers obtained at the B3LYP/6-31G(d)//CPCM level of theory; distances are in angstroms (Å). Color code by atom: green carbon, blue nitrogen, white hydrogen.

Table S1. Parameters for the Langmuir, Freundlich and Sips isotherm models at different temperatures.

Aromatic compounds	T (K)	Langmuir model			Freundlich model			Sips model		
		q_{\max} (mmol/g)	b (L/mmol)	R^2	K_F (mmol ¹⁻ⁿ L ⁿ /g)	n	R^2	K_s (L/g)	n_s	R^2
benzene	298	2.267	3.665	0.902	2.004	0.489	0.802	152.801	2.718	0.943
	313	2.834	4.418	0.898	2.640	0.466	0.795	217.795	2.483	0.954
	328	4.144	4.277	0.936	4.053	0.511	0.879	357.915	2.313	0.967
aniline	298	2.746	3.405	0.939	2.592	0.558	0.875	153.650	2.497	0.960
	313	3.909	2.502	0.960	3.455	0.635	0.927	188.385	2.496	0.956
	328	4.221	2.955	0.953	3.978	0.611	0.912	431.406	2.662	0.963
naphthylamine	298	2.956	6.050	0.995	3.275	0.482	0.962	18.024	1.037	0.994
	313	5.421	3.100	0.972	5.381	0.615	0.992	7.608	0.681	0.988
	328	5.932	3.383	0.960	6.070	0.599	0.976	8.568	0.672	0.971

Table S2. Summary of adsorbate properties (MW: molecular weight; pKa: dissociation constant; K_{OW} : octane-water distribution coefficient; π^* : solute π -polarity ability; β_m : hydrogen-bonding acceptor ability; α_m : hydrogen-bonding donor ability; S_w : solubility in water).

Chemicals	MW (g/mol)	pKa (mL/mol)	Log K_{ow}	π^*	β_m	α_m	S_w (mmol/L)
benzene	78.11 ^a	9.95 ^a	2.17 ^a	0.59 ^d	0.10 ^d	0.00 ^d	22.4 ^a
aniline	93.13 ^b	4.60 ^b	0.95 ^b	0.73 ^d	0.50 ^d	0.26 ^d	366.8 ^b
naphthylamine	143.2 ^c	3.92 ^c	2.222 ^c	0.83 ^d	0.50 ^d	0.31 ^d	11.87 ^c

a: W. Chen, L. Duan and D. Q. Zhu, *Environ. Sci. Technol.*, 2007, **41**, 8295-8300.

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Table S3. The mixture content of simulation samples. (mmol/L)

No.	1	2	3	4	5	6
Ben	0.1	0.2	0.3	0.4	0.2	0.3
BN	0.18	0.09	0.09	0.36	0.45	0.27
NA	0.06	0.24	0.18	0.06	0.12	0.30